Offprinted from Trans. Comm. II & IV, Int. Soc. Soil Sci., Aberdeen 1966

MOBILITY OF TRACE ELEMENTS IN DELTAS

(A study of pedogenesis relevant to availability problems)

A. J. de Groot

Institute of Soil Fertility, Groningen, Netherlands

SUMMARY

Sediments in deltaic areas on their way from the river to the sea can undergo changes in their trace-element composition by mobilization of these elements as soluble metallo-organic complexes. The amount of mobilization depends on the kind of element (Fe>Cu>Co>Mn) and on the quantity and decomposability of organic matter. Depending on the richness of the relevant river in trace elements, organic-matter regime in the delta, and distance from the river marginal or submarginal conditions for plant nutrition may appear in soils embanked from the delta. The latter is demonstrated in the case of copper.

INTRODUCTION

In deltaic systems there is a more or less constant transport of sand and fine-grained material from the rivers via the fresh-water tidal area to the near-by coast. Especially the fine-grained sediments with diameters less than 50 microns can move with the river and sea water in restricted times over large distances.

Much information has been obtained about the transport of the fine fractions in a number of deltas in western Europe and in some tropical regions in earlier work (De Groot 1963, 1964, 1966). The transport of mud (fine-grained fractions < 16 microns) has been investigated by the use of manganese as an accompanying element. The deposits from different rivers can be distinguished by different Mn contents. For instance, the Mn content of the mud of the river Elbe is seven times the amount of the river Thames. During transport in aerated river or sea water the mud cannot lose Mn, because the latter is almost exclusively present as insoluble higher oxides. After deposition reduction can take place, to a smaller or larger extent depending on the redox potential of the environment. Reduction of the sediment generally means loss of Mn, especially under marine conditions, caused by exchange of the Mn^{2+} ions by the salt ions. However, by gathering freshly deposited sediments (redox potentials about 400 mV) all over a deltaic system a full insight can be obtained of the distribution of the fine sediments from one or more sources (rivers or sea bottom) over the surrounding areas.

In this paper special attention will be paid to the behaviour of other trace elements (Fe, Cu, Co) during the movement of the fine-grained sediments on their way from the rivers through the deltas to the adjacent coastal areas. The direction of movement of the sediment in a given delta is known in this respect by the above-mentioned manganese studies, and has been published earlier.

Manganese studies in deltas in relation to movement of sediments are important for different reasons: studies of the genesis of soils derived from these sediments, knowledge of movement of sediments in connection with siltation of channels to harbours and the harbours themselves and, finally, the agricultural specialist needs information about quantities and texture of sediments he tries to gain in coastal areas for empoldering new land. In the latter case the knowledge of the manganese status of the empoldered land is also important in determining soil fertility.

The study of the behaviour of trace elements in a wider sense is important for both civil-engineering and agricultural reasons. The behaviour of trace elements naturally present in sediments can give information about the mobility of trace elements which have been artificially added to the mud for tracer studies concerning sediment-transport measurements. Trace elements with greater mobility are less suitable for such experiments. From an agricultural point of view these studies inform us about the trace-element status of Holocene soils, derived from mud sediments in deltaic systems. Depending on the trace-element contents in the original river material, the rates by which the trace elements dissolve from the suspended material into the surrounding water during transport (mobility of the elements), the distance of the agricultural area from the relevant river, as well as on the processes of soil genesis after sedimentation, the arable soils can contain trace elements in wide variations. In a number of cases this may lead to marginal conditions for plant growth. The latter will be explained specially for the case of copper.

METHODS OF INVESTIGATION

In connection with a preferred occurrence of the examined trace elements in the finest grain-size fractions, linear relationships are found between the contents of the different trace elements and the fraction <16 microns (as a percentage of the $CaCO_3$-free mineral constituents), if the location of the sediments is the same.

In Fig. 1 these relationships are demonstrated for Fe, Cu, Co and Mn in freshly deposited sediments of the river Ems (location Ditzum). The characterization of the trace-element status of the fine-grained fractions of a certain type of sediment is demonstrated, taking Mn as an example.

The relationships between the Mn content and the fraction <16 microns is extrapolated to 100% of the fraction <16 microns. An Ems deposit containing 35% of the fraction <16 microns, corresponds to the amount CE (= DF) of Mn in the fraction <16 microns and the amount EF in the sand fraction (>16 microns). Commonly the Mn composition of the fine fraction is represented by the line OA′. The extrapolated Mn content is represented by O′A′. For mutual comparison of sediments from different locations the contents O′A′ are used. Single values to characterize whole groups of cogenetic sediments with different granulometric compositions are thus obtained.

The coefficients of the regression equation

$$y_1 = \bar{a}x + \bar{b},$$

representing the relationship between the Mn content and the fraction <16 microns, are computed as follows:

$$\bar{a} = \frac{n\Sigma xy - \Sigma x \Sigma y}{n\Sigma x^2 - (\Sigma x)^2} \qquad \bar{b} = \frac{1}{n}(\Sigma y - \bar{a}\Sigma x)$$

where n represents the number of analysed samples; x and y are, respectively, the contents of the fraction <16 microns and the Mn contents of the samples concerned. The extrapolated Mn content O'A' ($y_{1\,100}$) is derived by substitution of the value $x = 100$.

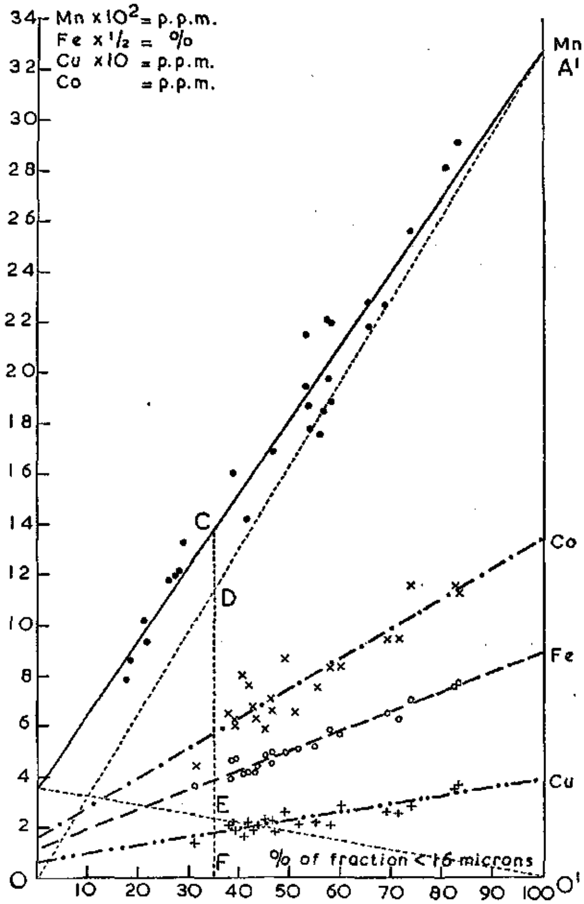

FIG. 1. Linear relationships between trace element contents and percentage of fraction <16 microns (Ems sediments).

In the accompanying tables the extrapolated values for the trace elements examined in sediments of the different locations in a number of deltas are tabulated.

The trace elements were removed from the sediments in the following way: Fe by boiling with 10% HCl, Cu and Co by boiling with a 1:1 mixture of conc. HNO_3 and conc. H_2SO_4, and Mn by treating the sediments with NH_4NO_3 at 550° and solution of the ash in HNO_3 1:1. The treatments mentioned do not guarantee total contents, but at any rate far more than the amounts normally active in pedogenetical processes.

EXPERIMENTAL RESULTS

In a number of deltas samples have been taken from freshly deposited sediments close to low-water level as well as from more elevated parts as forelands and young embankments.[1]

For each delta the samples were taken in a range from the inner part of the delta with fresh-water conditions to the outer marine environment as far as sediments from the relevant river could be detected by the applied manganese method. Trace-element determinations were carried out for studying changes in composition depending on the locations. Crops from the forelands and young embankments were analysed for Cu.

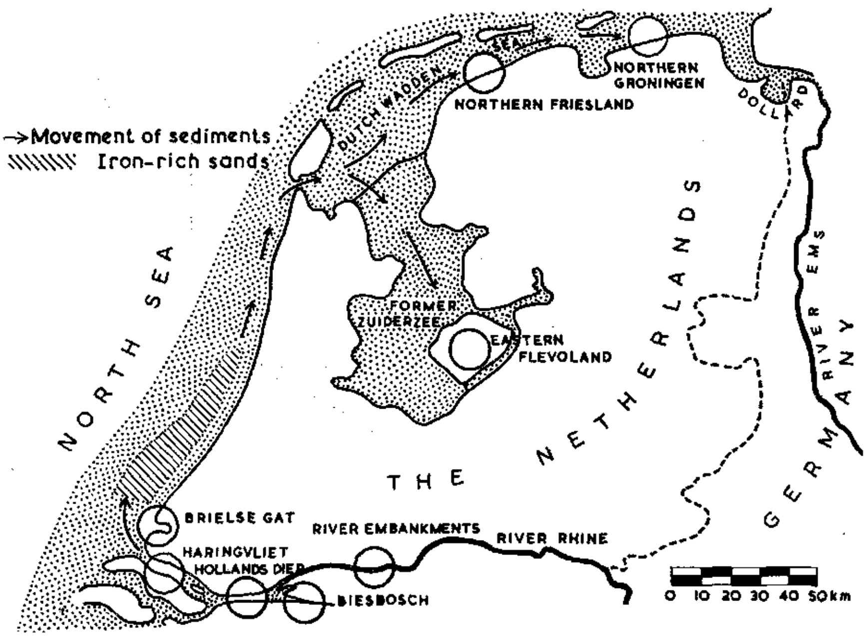

FIG. 2. Rhine delta (Netherlands).

Rhine delta (Netherlands)

The Rhine transports its fine-grained sediments by way of the fresh-water tidal area Biesbosch and along the Haringvliet in a northerly direction into the Dutch Wadden Sea (Friesland and Groningen), as indicated in Fig. 2.

The trace-element contents of sediments and crops are given in Table 1.

[1] In this article the term embankment denotes the forelands enclosed.

TABLE 1

Contents of trace elements in sediments (extrapolated to 100% of the fraction <16 microns) and contents of Cu in crops (mean values)
Rhine delta (Netherlands)

Location	Fresh mud					Foreland		Young embankments		
	Water	Sediments				Soils	Crops	Soils	Crops	
							Grass		Grass	Wheat
	‰ Cl	p.p.m. Mn	p.p.m. Co	p.p.m. Cu	% Fe	p.p.m. Cu	p.p.m. Cu	p.p.m. Cu	p.p.m. Cu	p.p.m. Cu
River embankments	0	—	—	—	—	—	—	—	17	—
Biesbosch	0	2601	24	470	7·75	387	34	73	15	18
Hollands Diep	<0·5	—	—	—	—	—	22	—	—	—
Haringvliet	2	2572	18	183	3·69	—	17	—	—	—
Brielse Gat	—	2583	18	146	3·29	—	13	—	—	—
Northern Friesland	16	2632	10	53	3·16	49	10	38	12	—
Northern Groningen	16	1762	—	—	3·47	41	12	36	10	9
Eastern Flevoland	—	—	—	—	—	—	—	33	10	9

From the river down to sea as far as Northern Friesland the Mn contents of the fresh mud samples remain constant, as a consequence of direct transport as an aerated suspension to the relevant locations. The Groningen sediments are supplied by the river Rhine, but have lost part of their Mn in consequence of earlier temporary deposition along the Friesian coast (temporary reduction of the sediment with loss of Mn^{2+} ions by exchange reactions).

The other elements undergo to a varying extent losses during passage of the sediments to the lower courses of the delta.

The most striking in this respect is Fe, which already reaches almost its lowest state in the Haringvliet. The Cu contents also undergo intensive decreases which, however, need a longer distance to reach the lowest values. Finally, Co reaches a more intense mobilization not before the marine area along the Dutch Wadden coast (Friesland) and must therefore be seen as the least mobile element in this respect.

During transport of the sediments to the lower courses of the delta an intensive decomposition of organic matter takes place. On the relative short distance from the Biesbosch to the Haringvliet the content diminishes from 29 to 22% (values extrapolated to 100% of the fraction <16 microns, as has been done for the trace-element contents), from the Haringvliet to Friesland a further decrease to 16% takes place. The C/N ratios of the organic matter at these three locations were 21, 14 and 11, respectively. The largest decrease in organic-matter content and the most drastic qualitative change (C/N ratio) takes place on the reach where the mobilization of trace elements is most intense (from Biesbosch to Haringvliet). Already the above-mentioned behaviour of the organic matter indicates the mobilization of trace elements as organometallic compounds.

The great mobilization of Fe directly down the delta unmistakably leads to an enrichment of the surrounding water with Fe. After reaching the full marine environment, part of this iron is reflocculated on sand grains on the sea bottom. EISMA (*1966*) discovered a tongue of iron-rich sands corresponding to the northern movement of Rhine water into the North Sea (indicated in Fig. 2).

Besides close to the low-water level, sedimentation can take place on the forelands, generally lying above mean high water. The sediments on these forelands have already undergone processes of pedogenesis and carry vegetation. From these forelands the young embankments have been derived.

The processes of soil genesis concerning the Cu contents will now be described for the more elevated sediments mentioned before.

From Table 1 it is clear that the Cu contents of the Biesbosch forelands have undergone an appreciable loss in comparison with the fresh muds. This must be seen in relation to the rather rapid conversion of organic material in the foreland area. A very intensive loss of Cu appears when the Biesbosch foreland is embanked. The embankment causes an enormous breakdown of organic matter (from 34 to 9%) with consequent qualitative alterations (C/N ratio from 20 to 13%) that explains the rapid fall in Cu contents.

Far down the delta (Friesland and Groningen) the Cu contents of the fresh mud are rather low. Pedogenesis on the foreland and subsequent embankment do not give rise to a further important decline of the Cu values. The breakdown of organic matter is rather slow in these fully marine regions.

From the forelands grass samples have been taken and from the young embankments grass and, as far as possible, wheat foliage from various strains. Sampling occurred under uniform conditions: length of grass 10 cm, and length of wheat 20 cm. The samples were analysed for total Cu content.

In Table 1 the Cu contents of the crops are given for the different locations as mean values of a large number of samples. It shows that the Cu contents of the crops are a clear reflection of the Cu status of the corresponding soils. The Cu contents of the grass on the forelands decrease more and more in the downward direction of the delta. The same applies to grass and wheat on young embankments, the trend being less pronounced, however, as a consequence of the large loss of Cu by embanking soils from the forelands in the upper deltaic area (Biesbosch).

A content of 7 p.p.m. of Cu in pasture grass is generally considered adequate for cattle (experience in different countries). The mean values presented in Table 1 are still well above this level, but in a number of cases the individual contents are lower than 7 p.p.m. Moreover, it is not impossible that, especially in the lower part of the delta, deficiency will generally occur in the long run if no copper fertilizer is supplied.

It is impossible to give precise limiting values as to the Cu content of wheat foliage (Reith and Mitchell 1964; Smilde 1966). Seedlings well supplied with Cu contain 4–10 p.p.m. Cu when sampled at a height of 20 cm. In the lower part of the delta (Groningen and Flevoland) the mean Cu contents of wheat foliage are lower than the upper limit of 10 p.p.m. for certain strains, so special control of the Cu supply is necessary.

A special comment may be added about Eastern Flevoland. This important agricultural area, derived from sediments transported by the Rhine to the former Zuiderzee, was embanked in 1956. Even in this young polder the Cu contents in crops are marginal or submarginal.

Ems delta (Germany)

The Ems transports its sediments by way of the fresh-water tidal area Diele to the Dollard (Figs. 2 and 3). The trace-element contents of sediments and crops are given in Table 2.

The Mn contents of the fresh mud remain constant from Diele as far as the German Dollard, pointing to pure Ems deposits within this range. In the Dutch Dollard area an admixture takes place with Rhine sediments, entering from the Dutch Wadden Sea, and giving rise to lower Mn contents.

The sequence of mobilization down the delta of the other trace elements in the fresh mud is the same as for the river Rhine, although the mobilization processes take place within a much shorter distance than in the Rhine delta.

This may be partly caused by a longer residence of the suspension in the estuary of the river. The main cause must be attributed, however, to a more drastic behaviour of the organic matter with regard to the solubilization of trace elements. The decomposition of organic matter in the upper delta is more intensive than within the comparable range of the Rhine (contents at Diele, Leerort and Ditzum 29, 17 and 14%, respectively). The C/N ratios in the Ems estuary are much lower than in the Rhine and remain almost constant (12) during transport. There is a remarkably high cation-exchange capacity of the organic matter from the Ems.

TABLE 2

Contents of trace elements in sediments (extrapotaled to 100% of the fraction <16 microns) and contents of Cu in crops (mean values)
Ems Delta (Germany)

Location	Fresh mud					Foreland		Young embankments		
	Water	Sediments				Soils	Crops	Soils	Crops	
							Grass		Grass	Wheat
	‰ Cl	p.p.m. Mn	p.p.m. Co	p.p.m. Cu	% Fe	p.p.m. Cu	p.p.m. Cu	p.p.m. Cu	p.p.m. Cu	p.p.m. Cu
Diele	0	—	22	147	11·20	75	14	75	13	—
Leerort	<0·3	3262	17	49	5·32	—	11	—	—	—
Jemgum	<0·3	—	—	—	—	—	11	—	—	—
Ditzum	6	3262	39	13	4·43	40	11	24	9	9
German Dollard	>6	3143	9	33	3·64	—	9	24	9	11
Dutch Dollard	>6	2081	11	36	3·70	—	9	29	11	9

Forelands and young embankments show an equal trend in soil and crop contents of Cu as the Rhine delta, the foreland at Diele (fresh-water tidal area) having lost, however, relatively even more Cu than the comparable part of the Rhine delta. The latter may be attributed again to the highly solvent action of the organic matter of the river Ems. The young embankments at Diele have Cu contents of the same order as the forelands. This is caused by the fact that these embankments have the character of summer polders, receiving regularly fresh mud deposits from the river.

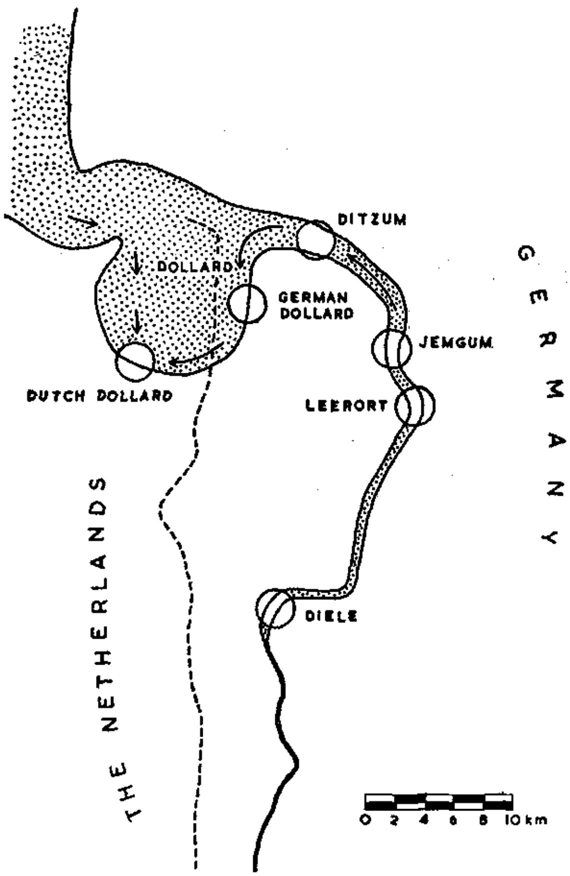

FIG. 3. Ems delta (Germany) → Movement of sediments.

In the marine area at Ditzum and in the Dollard the Cu contents of crops are as low as in the lower part of the Rhine delta, giving rise to marginal or submarginal conditions.

The somewhat higher Cu contents in muds and soils of the Dutch Dollard will be caused by the above-mentioned influence of the Rhine in this part of the delta.

Chao Phya delta (Thailand)

Instructed by the Thailand office of the Netherlands Engineering Consultants (NEDECO), investigations have been carried out in which the Mn method has been used for studying the movement of mud from the Chao Phya to the bar of the river in the Bay of Thailand. These investigations were carried out in connection with siltation problems of the harbour of Bangkok (De Groot 1965).

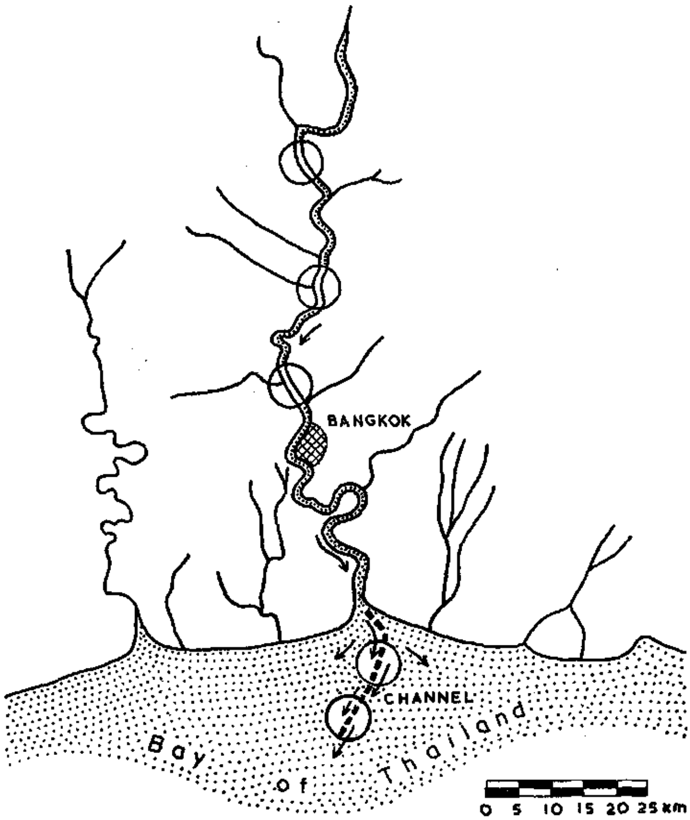

FIG. 4. Chao Phya delta (Thailand) → Movement of sediments.

The Mn contents and the subsequent estimated contents of other trace elements from locations in the fresh-water tidal area of the river as well as from a fully marine area in the bay (channel to the river mouth) are given in Table 3. The geographical data are shown in Fig. 4.

The Mn contents in the channel are lower than those of the river, caused by reduction and subsequent exchange of Mn^{2+} ions. The Fe, Cu and Co contents of the fine-grained sediments, however, remain nearly constant during movement downwards the delta.

The sharp contrast in mobility of trace elements in the above-mentioned deltas under temperate climatic conditions and this tropical delta must also be attributed to the behaviour of the organic matter. During transport of sediments to the lower courses of the Chao Phya delta the very low organic-matter contents of the river hardly decrease (from 3·8% in the river to 3·0% in the channel). The question arises to what extent principal differences exist in this respect between deltas under temperate and tropical climatic conditions. This aspect needs further experimental evidence.

TABLE 3

Contents of trace elements in sediments (extrapolated to 100% of the fraction <16 microns)
Chao Phya delta (Thailand)

Location	Fresh mud				
	Water	Sediments			
	‰ Cl	p.p.m. Mn	p.p.m. Co	p.p.m. Cu	% Fe
River	0	1811	12	50	3·95
Channel	14	1320	13	44	4·04

DISCUSSION ON THE MOBILIZATION OF TRACE ELEMENTS

It is impossible to give sufficient experimental background on the chemical details of the mobilization processes of trace elements in deltas in this publication. More experimental evidence will be given in a later paper.

From an experimental point of view we only give in Table 4 the contents of organic Fe and Cu, being the most mobile metals, as mean values for freshly deposited mud samples from a number of locations down the Ems delta.

The organic-Fe contents of the mud have been estimated by extracting the samples at pH 7·5 with a solution of ethylenediamine-N, N′-bis(o-hydroxyphenyl acetic acid), generally abbreviated to EDDHA, with and without the presence of H_2O_2. The ligand EDDHA forms very stable chelates with Fe^{3+} ions, thus competing with Fe bound by natural chelating compounds. Besides chelating properties, the ligand has a reducing effect, however, on freshly precipitated iron hydroxides, the latter being prevented by the addition of H_2O_2.

The organic-Cu contents could be determined by extraction of the mud samples at pH 7·5 with a solution of triethylenetetramine (trien), a ligand specific for Cu chelation.

Table 4 shows that both organic-Fe and -Cu contents in the mud decrease downwards the delta, thus showing diminishing mobility in the direction of the sea. The same trend has been found for the Rhine delta. Although the trace-element contents in question refer to insoluble organic compounds in the mud, they are expected to reflect the contents of organometallic compounds soluble in the surrounding river or sea water. In this connection a well known fact in soil chemistry may be mentioned: that metal chelates are more soluble as the metal-ligand ratios are lower.

In the lower part of the delta (Ditzum) the Fe dissolved by EDDHA is higher in the presence of H_2O_2 than without addition of the oxidizing agent. In a separate investigation it became evident that H_2O_2 modified a fraction of Fe-organic compounds, which themselves were not soluble in EDDHA.

The greater mobility of Fe in sediments from the fresh-water part of the delta as compared with the marine area can also be shown by the amounts of Fe exchangeable with NH_4-acetate solutions, being easily measurable under fresh-water conditions and extremely low in the salt water.

TABLE 4

Contents of Fe and Cu as organic compounds in sediments from the Ems delta

Location	Fresh mud			
	Water	Sediments		
	‰ Cl	‰ Fe without H_2O_2	‰ Fe with H_2O_2	p.p.m. Cu
Diele	0	4·6	3·6	24
Grotegaste	<0·3	—	—	13
Oldendorp	6	—	—	11
Ditzum	6	0·8	2·1	—

Concerning the contrast between the behaviour in mobility of trace elements in muds from the tropical Chao Phya and the European rivers a few words may be devoted to unpublished work of the author on the Co-fixation capacity of sediments from the rivers mentioned. Samples from the fresh-water tidal areas of the Rhine and Ems are able to bind quantities of Co far exceeding the exchange capacity of the material. It has been pointed out in detailed investigations that most of the Co was present as chelate compounds. Sediments from the fresh-water part of the Chao Phya river, however, only tied up Co in quantities slightly exceeding the exchange capacities of these materials. Thus more experimental evidence has been obtained of the possibility that the organic matter is active in mobilizing trace elements as chelate compounds.

There is much evidence in the literature on the existence of metal chelates in soils and their role in pedogenesis. The author gave in an earlier publication a compilation on this work, supplemented by his own experiences (De Groot 1963). Within the scope of the present paper attention will only be paid to the well known rule of Irving and Williams on the relative stabilities of chelates of various metals (Irving and Williams 1948). Selecting from this rule those metals which have been examined in our investigations (sequence of stabilities $Fe^{3+} > Cu^{2+} > Co^{2+} > Mn^{2+}$), we find the same order in the measure in which the elements become mobile with the decomposing organic matter. The conclusion may be drawn that the stability of the organometallic compounds in deltaic systems is the dominating factor in the mobilization processes.

REFERENCES

Eisma, D. 1966. Iron and trace elements in Dutch coastal sands. Neth. J. Sea Res. **3**, 68–94.

Groot, A. J. de. 1963. Mangaantoestand van Nederlandse en Duitse holocene sedimenten. Versl. landbouwk. Onderz. 69, 7, 1–164.

Groot, A. J. de. 1964. Origin and transport of mud in coastal waters from the Western Scheldt to the Danish frontier. Developments in Sedimentology (Amsterdam) **1**, 93–103.

Groot, A. J. de. 1965. *In* Siltation Bangkok Port Channel. NEDECO (The Hague) **2**, 344–356

Groot, A. J. de. 1966. Mud transport studies using manganese as an accompanying element under temperate and tropical climatic conditions. Proc. Dacca Symp. (UNESCO) Sci. Probl. Humid trop. Zone Deltas, pp. 65–71.

Irving, H. and Williams, R. 1948. Order of stability of metal complexes. Nature **162**, 746–747.

Reith, J. W. S. and Mitchell, R. L. 1964. The effect of soil treatment on trace element uptake by plants. Plant Anal. Fert. Probl. **4**, 241–254.

Smilde, K. W. 1966. The sensitivity of various cereals and strains of cereals to copper deficiency. (In press.)